Recent Developments in the Main Group Element Chemistry (SYNTHETIC ORGANIC CHEMISTRY-Synthetic Design)

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Kohei Tamao, Akio Toshimitsu, and Shigehiro Yamaguchi

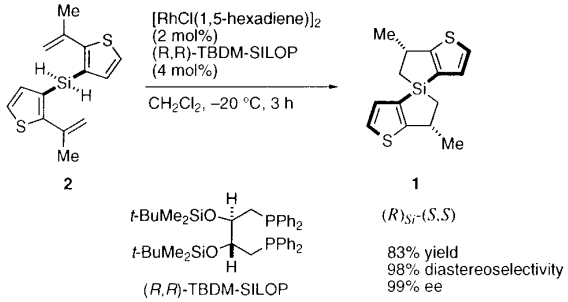
Some recent advances in the main group element chemistry, especially in the organosilicon chemistry and the organoselenium chemistry, are described herein as follows: (1) Asymmetric intramolecular hydrosilation yielding an optically pure spirosilane with axial chirality, (2) high electron-transporting abilities of new silole π-conjugated compounds, and (3) effective steric protection of the selenium atom of the episelenonium ion intermediate.

Keywords: Spirosilanes / Asymmetric intramolecular hydrosilation / Silole / Electron-transporting materials / Organic electroluminescent devices / Episelenonium ion / 2,4,6-Tri-*tert*-butylphenyl group

1. Axially Chiral Spirosilanes via Catalytic Asymmetric Intramolecular Hydrosilation [1].

Chiral spiranes having axially chirality are of special interest due to their rigid chiral environments of C_2 symmetry by perpendicularly arranging two planes. The spiranes would thus be promising chiral building units for material science, especially for chiral macromolecules such as molecular squares and polymers with main-chain chirality. However, there is only a limited number of optically pure spiranes available, because optical resolution has been the only methodology to attain them. To the best of our knowledge, asymmetric syntheses of the axially chiral spiranes have rarely been reported. We now report the first catalytic asymmetric synthesis of an axially chiral spirane of C_2 symmetry.

As the chiral spirane, we have designed a 5-silaspiro[4.4]nonane derivative **1** having a silicon atom on the



spiro center and two thiophene rings fused with the spiro[4.4]nonane skeleton. The spirosilane **1** has been successfully prepared via a Rh(I)-catalyzed intramolecular hydrosilation of bis(alkenyl)dihydrosilane **2**. The intramolecular hydrosilation of **2** would proceed sequentially in two steps: The first step involves a diastereotopic group selection and diastereotopic face selection, producing a chiral

SYNTHETIC ORGANIC CHEMISTRY —Synthetic Design—

Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel π-conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfoniu and episelenonium ions.

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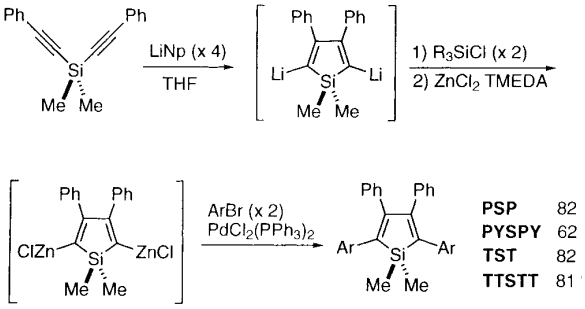
center on the silicon atom as well as on a carbon atom. The second intramolecular hydrosilation is a simple diastereotopic face selection of the remaining olefin to carry the third chiral center on the carbon atom. In total, three pairs of enantiomers are possible. The asymmetric intramolecular hydrosilation in the presence of a Rh(I) complex with (*R*,*R*)-SILOPs, which have now been introduced by us as new C_2 symmetry chiral bidentate ligands, have afforded one of the six enantiomers as the major product with high diastereoselectivities up to 98 % and high enantiomeric excesses up to 99 %.

2. Silole Derivatives as Efficient Electron Transporting Materials [2].

Organic electroluminescent (EL) devices, generally composed of thin multilayers of hole transporting (HT), emissive, and electron transporting (ET) materials sandwiched between two electrodes, are enjoying a great deal of interest because of their possible application as large-area flat panel displays. One of the major current subjects in this field is the development of efficient ET materials. Here, several new 2,5-di(aryl)silole derivatives having 3-methylphenyl (PSP), 2-pyridyl (PYSPY), 5-*tert*-butyldiphenylsilyl-2-thienyl (SiTSTSi), and bithienyl (TTSTT) as aryl groups have been examined as electron transporting (ET) materials for thin multilayer organic electroluminescent devices. The silole



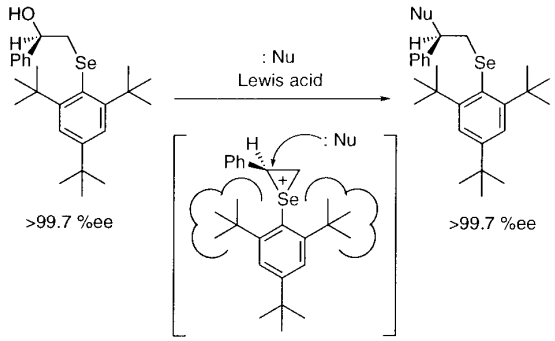
derivatives have been prepared in one pot starting from bis(phenylethynyl)silane based on an intramolecular reductive cylization promoted by lithium naphthalenide, followed by a palladium-catalyzed coupling reaction with appropriate aryl halides. Among these silole derivatives, PYSPY shows the highest ET ability, which also exceeds that of tris(8-hydroxyquinoline)aluminum (Alq), one of the best ET materials. Three other silole derivatives are found to act as emissive ET materials, emitting greenish-blue to reddish-orange lights with the colors being tuned with the aryl groups.

3. Steric Protection of the Selenium Atom of the Episelenonium Ion Intermediate To Prevent both the Racemization of the Chiral Carbon and the Selenophilic Attack of Carbon Nucleophiles [3].

Organic reactions *via* the three-membered cyclic episelenonium ion intermediate have been widely used in organic syntheses. Still, two basic drawbacks of the episelenonium ion intermediate have remained to be solved. Thus, in the episelenonium ion intermediate bearing a phenyl group on the selenium atom, (1) a chiral carbon present in the three-membered ring racemizes quite readily during reactions and (2) carbon nucleophiles such as ketene silyl acetals attack the selenium atom selectively rather than the carbon atom to give no carbon–carbon bond formation products. We have found that these drawbacks are both overcome by the steric protection of the selenium atom by 2,4,6-tri-*tert*-butylphenyl (TTBP) group.

Our strategy is based on our observation that the rate of racemization of the chiral carbon in the episelenonium ion intermediate is highly dependent on the concentration of the substrates, the arylseleno-substituted alcohol, indicating that the racemization is induced by the selenophilic attack on the selenium atom of the intermediate by the alcohol.

In fact, as shown in below, chiral alcohol bearing the TTBPSe group on the adjacent carbon atom was found to react with carbon nucleophiles such as alkenyl silyl ethers, trimethylsilyl cyanide, and allyltrimethylsilane in the presence of Lewis acid to afford the carbon–carbon bond formation products in satisfactory yields without loss of optical purity.



References

1. Tamao K, Nakamura K, Ishii H, Yamaguchi S and Shiro M, *J. Am. Chem. Soc.*, **118,** 12469 (1996).
2. Tamao K, Uchida M, Izumizawa T, Furukawa K and Yamaguchi S, *J. Am. Chem. Soc.*, **118**, 11974 (1996).
3. Toshimitsu A. Nakano K. Mukai T. and Tamao K. *J. Am. Chem. Soc*., **118**, 2756(1996).